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## 1. AGENCY

Sept. 27, 1991

3. REPORT TYPE AND DATES COVERED  
Final 8-1-88 to 7-31-91

## 4. TITLE AND SUBTITLE

Derivatives of Boranes, Possible Metal and Boride and  
Boron Nitride Precursors

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## 6. AUTHOR(S)

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S ELECTE  
JAN 09 1992  
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## 5. FUNDING NUMBERS

DAAL03-88-K-0176

(2)

## 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS

The Ohio State University Research Foundation  
1960 Kenny Rd  
Columbus, Ohio 432108. PERFORMING ORGANIZATION  
REPORT NUMBER

## 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office  
P. O. Box 12211  
Research Triangle Park, NC 27709-221110. SPONSORING/MONITORING  
AGENCY REPORT NUMBER

ARO 26/45.11-CH

## 11. SUPPLEMENTARY NOTES

The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

## 12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

## 12b. DISTRIBUTION CODE

## 13. ABSTRACT (Maximum 200 words)

The synthesis of  $B_{10}H_{14}$  from  $B_3H_9$  was modified to facilitate large scale production. Reductions of boranes by alkali and lanthanide metals were studied. Depending upon reaction conditions chosen, the anions  $[BH_3]^{2-}$ ,  $[B_2H_6]^{2-}$ , and  $[B_3H_8]^-$  were produced. A simple procedure was developed for the preparation of the solvent free salts  $M[B_3H_8]$  ( $M = K, Rb, Cs$ ). Borohydrides of the divalent lanthanides Yb, Eu were synthesized, structurally characterized, and then converted to lanthanide borides  $YbB_4$  and  $EuB_6$ . New procedures for the preparation of high purity boron nitride as powders and coatings were developed. An essentially instantaneous reaction between  $B_3N_3H_3Cl_3$  and Cs can be initiated at temperatures as low as 135 °C to produce very finely divided amorphous boron nitride. The amorphous BN is converted to the turbostratic form by heating it at 1100 °C.  $H_3NBH_2Cl$  in solution form can be applied to a surface. Heating to 1100 °C in vacuum produces a coating of turbostratic BN.

## 14. SUBJECT TERMS

decaborane, borane anions, lanthanide borohydride,  
lanthanide boride, boron nitride

## 15. NUMBER OF PAGES

16

## 16. PRICE CODE

17. SECURITY CLASSIFICATION  
OF REPORT

UNCLASSIFIED

## 18. SECURITY CLASSIFICATION

UNCLASSIFIED

19. SECURITY CLASSIFICATION  
OF ABSTRACT

UNCLASSIFIED

## 20. LIMITATION OF ABSTRACT

UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)  
Prescribed by ANSI Std Z39-18  
298-102

92 1 7 089

**DERIVATIVES OF BORANES, POSSIBLE METAL BORIDE AND BORON NITRIDE PRECURSORS**

**Final Report**

**For the Period**

**August 1, 1988 - July 31, 1991**

**Dr. Sheldon G. Shore**

**September 27, 1991**



**U. S. ARMY RESEARCH OFFICE  
Research Triangle Park, North Carolina 27709**

**ARO Proposal No. 26145-CH**

**Grant No. DAAL03-88-K-0176**

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**The Ohio State University Research Foundation**

## FORWARD

The period in which this grant was in effect was one of transition in this laboratory. The focus of our program shifted from investigations of boron hydrides to a more general one that also encompasses investigations of boron nitrogen and lanthanide boron containing materials. While continuing with boron hydride syntheses, significant progress was made in these newer areas.

Our studies equally emphasize new, novel chemistry; efficient synthetic procedures adaptable to scale-up; and practical applications of results. Our earlier work under ARO support led to the syntheses of high purity electronics grade diboranes,<sup>1a</sup>  $B_2H_6$  and  $B_2D_6$ , which are now commercially produced by the Voltaix Company. High purity deuterated diborane is receiving very favorable attention for applications in plasma fusion reactors. We also developed a number of practical syntheses of higher boranes,<sup>1b-8</sup> including  $B_{10}H_{14}$ , using  $B_5H_9$  as a feed stock, thus enabling the conversion of surplus  $B_5H_9$ , in U.S. Government stockpiles (ca. 200,000 lbs) to more useful materials.

During our present grant period we modified our procedure for the conversion of  $B_5H_9$  to  $B_{10}H_{14}$  in order to make it more convenient for large scale production. No longer commercially produced in the United States,  $B_{10}H_{14}$  is in short supply. Strem Chemical Company has been able to duplicate our procedure and is currently working out details for production in kilo quantities. The Transbas Company is also interested in our procedure. Other examples of technology developed in this laboratory, during the period of this grant, are our preparations of high purity boron nitride powders<sup>38</sup> and coatings.<sup>39</sup> These procedures are presently under consideration by Union Carbide Corporation, Advanced Ceramics Division.

Our research activities are summarized in the following sections which are listed in the Table of Contents. Each section contains a preamble which provides a statement of the problem studied.

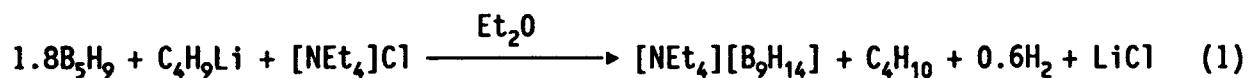
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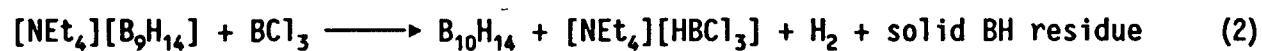
## I. MODIFIED SYNTHESES OF $[B_9H_{14}]^-$ SUITABLE FOR LARGE SCALE PRODUCTION OF $B_{10}H_{14}$

In earlier grants under ARO support we demonstrated that  $B_5H_9^{1b-4}$  can be successfully employed in close to quantitative preparation of either  $[B_9H_{14}]^-$  or  $[B_{11}H_{14}]^-$ , depending upon the conditions chosen. We were able to convert these anions to  $B_{10}H_{14}$  and a number of higher boron hydride derivatives. Thus the  $B_5H_9$  presently in U.S. Government storage can be converted to potentially useful materials.

With the present shortage of  $B_{10}H_{14}$  due to the absence of commercial production in the U.S., we developed a modification of our earlier synthesis of  $[B_9H_{14}]^-$  that would be more suitable for large scale production of this anion, which in turn would facilitate large scale production of  $B_{10}H_{14}$ . In our earlier work we generated  $[B_9H_{14}]^-$  by deprotonating  $B_5H_9$  with NaH in the presence of  $[NEt_4]Cl$  in THF. However, it is impractical to use NaH on a large scale since it must first be removed from its protective oil packing and then cleaned. We were able to substitute butyl lithium for NaH as the deprotonating agent as shown in Equation (1). The synthesis of  $B_{10}H_{14}$  from  $[B_9H_{14}]^-$  in about 60% yield was achieved



according to our usual procedure as indicated by Equation (2).



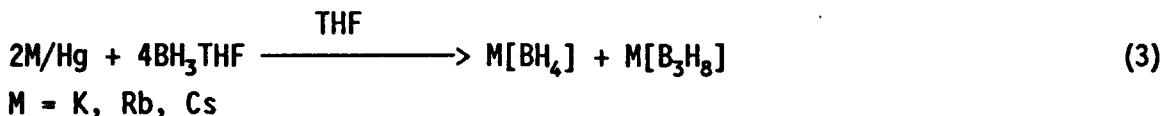
The Strem Chemical Company has repeated our modified procedure and is scaling it up with a view to commercial production. The Transbas Company of Billings, Montana is also interested in our procedure. The modified synthesis of  $[B_9H_{14}]^-$  can also lead to the scaled up syntheses of higher borane derivatives that we have prepared from this anion.<sup>1b-8</sup>

## II. FORMATION OF SOLVENT FREE ALKALI METAL (K, Rb, Cs) SALTS OF $[B_3H_8]^-$

Applications of the octahydrotriborate(1-) ion,  $[B_3H_8]^-$ , include: explosive and propellant technology;<sup>9</sup> preparation of electrode coatings<sup>10</sup>; neutron capture therapy;<sup>11</sup> serum triglyceride and serum cholesterol biological studies;<sup>12</sup> syntheses of metallaboranes,<sup>13</sup> higher borane<sup>14</sup> heteroatom boranes<sup>15</sup> and carborane cluster compounds;<sup>16</sup> and reduction of a number of organic compounds.<sup>17</sup>

Prior to our work, no *simple* route to solvent free alkali metal salts of  $[B_3H_8]^-$  was reported.  $Na[B_3H_8]$  is highly solvated by ether,<sup>18</sup> making it difficult to accurately measure amounts of this salt to be used for chemical reactions. It is generally converted to more tractable alkylammonium,<sup>19,20</sup> alkylphosphonium,<sup>21</sup> other alkali metal<sup>19</sup> or thallium<sup>19b</sup> salts by metathesis reactions.

We obtained the salts  $M[B_3H_8]$  ( $M = K, Rb, Cs$ ) through the reduction of  $BH_3THF$  by alkali metal amalgams.<sup>22</sup> This procedure provides a solvent free



product, and provides simpler routes to these salts than previously described.<sup>19</sup> Furthermore, for most, if not all applications,  $Tl[B_3H_8]$  can be replaced by one of the alkali metal  $[B_3H_8]^-$  salts described here.  $Tl[B_3H_8]$  is a useful material in the preparation of derivatives of  $[B_3H_8]^-$  through metathesis reactions,<sup>19</sup> but because of the toxicity of thallium,<sup>23</sup> this salt presents a hazard.

In the present grant period we took advantage of our synthesis of solvent free  $K[B_3H_8]$  by simplifying our procedure for the synthesis of  $B_4H_{10}$  by substituting  $K[B_3H_8]$ <sup>22</sup> for  $[NEt_4][B_3H_8]$  (Equation (4)). Our earlier procedure<sup>3</sup>

$$K[B_3H_8] + BC1_3 \longrightarrow B_4H_{10} + K[HBC1_3] + \text{solid BH residue} \quad (4)$$

required the preparation of  $[NEt_4][B_3H_8]$  from  $Na[B_3H_8]$  because Equation (4) is not

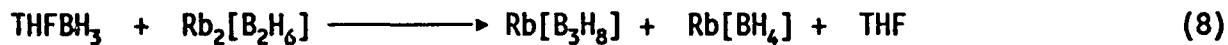
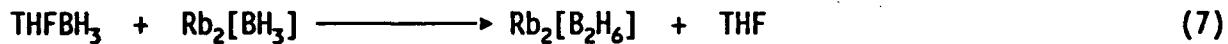
effective with  $\text{Na}[\text{B}_3\text{H}_8]$  due to retained ether interfering with the desired reaction between the  $[\text{B}_3\text{H}_8]^-$  anion and the boron halide. Prior to this reaction, solvent free alkali metal salts of  $[\text{B}_3\text{H}_8]^-$  required multi-step procedures.<sup>19</sup>

### III. FORMATION OF $[\text{BH}_3]^{2-}$ AND $[\text{B}_2\text{H}_6]^{2-}$

In the preceding grant period we showed that the homogeneous reduction of  $\text{BH}_3\text{THF}$  by an alkali metal, in the presence of naphthalene as an electron carrier, can produce  $[\text{BH}_3]^{2-}$ , the analogue of the carbanion  $[\text{CH}_3]^-$ . This is in contrast to the synthesis of  $[\text{B}_3\text{H}_8]^-$  described above which is a heterogeneous reaction involving alkali metal amalgams. In the present grant period studies of the homogeneous reduction reaction were continued. Addition of  $\text{BH}_3\text{THF}$  to  $[\text{BH}_3]^{2-}$  gives  $[\text{B}_2\text{H}_6]^{2-}$ , the analogue of  $\text{C}_2\text{H}_6$ . The  $[\text{B}_2\text{H}_6]^{2-}$  dianion is converted to  $[\text{B}_3\text{H}_8]^-$  and  $[\text{BH}_4]^-$  upon addition of two moles of  $\text{BH}_3\text{THF}$ . The following reaction sequence was studied. The anions produced in these reactions are stable in the absence of air.



$\text{M} = \text{Na, K, Rb, Cs}$



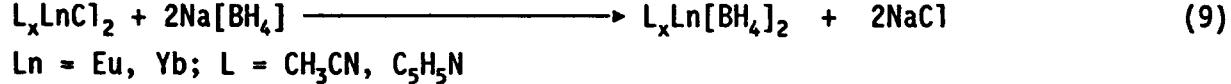
### IV. LANTHANIDE-BORANE COMPLEXES AS PRECURSORS TO LANTHANIDE BORIDES

Borides of the lanthanides, transition metals, and actinides are extremely hard, wear resistant materials that can possess desirable magnetic, electronic, thermal, and mechanical properties.<sup>24</sup> During the present grant period we studied borane derivatives of divalent lanthanides that are potential precursors to lanthanide borides. We produced new materials and demonstrated that several of them are readily converted to lanthanide borides and coatings. Described below

is a summary of our work.

### A. Syntheses of Borohydride Complexes of Eu(II) and Yb(II)

We find<sup>25</sup> that  $\text{CH}_3\text{CN}$  and  $\text{C}_5\text{H}_5\text{N}$  are exceptionally good ligands for promoting formation of complexes of  $\text{Ln(II)}$  with boron hydride anions. A series of Eu(II) and Yb(II) borohydride complexes were synthesized, isolated, and characterized:  $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu\text{-H})_3\text{BH}]_2$ ,  $(\text{C}_5\text{H}_5\text{N})_4\text{Yb}[\text{BH}_4]_2$ ,  $(\text{CH}_3\text{CN})_2\text{Eu}[\text{BH}_4]_2$ , and  $(\text{C}_5\text{H}_5\text{N})_{1.8}\text{Eu}[\text{BH}_4]_2$ . Equation (9) represents the general reaction employed. Not only are coordination



$\text{Ln} = \text{Eu, Yb}; \text{L} = \text{CH}_3\text{CN, C}_5\text{H}_5\text{N}$

geometries of the metals of interest, but these complexes also serve as precursors to the formation of lanthanide borides (see section IV.C.).

Figure 1 shows structures of  $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu\text{-H})_3\text{BH}]_2$  and  $(\text{C}_5\text{H}_5\text{N})_4\text{Yb}[\text{BH}_4]_2$ .

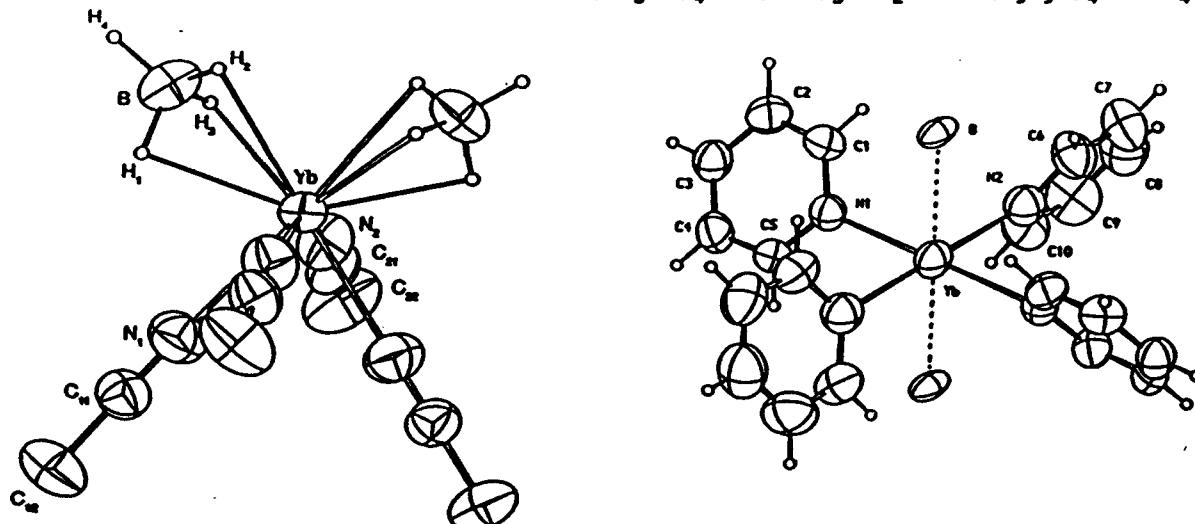


Figure 1. Molecular structures of  $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu\text{-H})_3\text{BH}]_2$  and  $(\text{C}_5\text{H}_5\text{N})_4\text{Yb}[\text{BH}_4]_2$ . Each borohydride unit in  $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu\text{-H})_3\text{BH}]_2$  is bound to Yb through three Yb-H-B bridges and the four  $\text{CH}_3\text{CN}$  ligands are arranged in a "see-saw" configuration with respect to the central Yb atom.

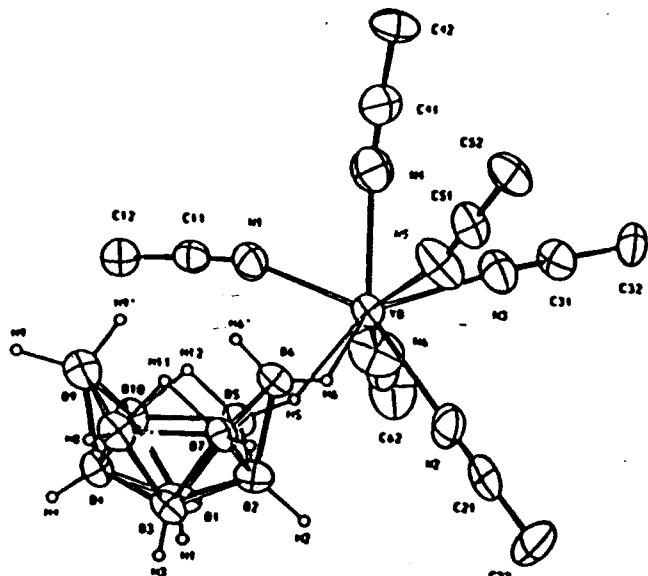
The structure of  $(\text{C}_5\text{H}_5\text{N})_4\text{Yb}[\text{BH}_4]_2$  contains an axially distorted octahedral arrangement of ligands around Yb(II). Borohydride ligands are *trans* to each other

along the elongated axis. Pyridine ligands are arranged in the shape of a "four-bladed propeller". Hydrogens on the borohydride could not be located in the X-ray structure determination; however, the bonding mode of  $[\text{BH}_4]^-$  is believed to be the same,  $\eta^3$ , in this compound as in  $(\text{CH}_3\text{CN})_6\text{Yb}[(\mu\text{-H})_3\text{BH}]$  since their Yb-B distances agree within 0.026(11) Å. Different hapticity of the borohydride ligand is expected to cause a significant difference in metal-boron distances.<sup>26</sup>

### B. Reduction of Decaborane(14) by Lanthanide-Ammonia Solutions

We found<sup>25b</sup> that liquid  $\text{NH}_3$  solutions of Eu and Yb, like liquid  $\text{NH}_3$  solutions of Na<sup>27</sup>, reduce  $\text{B}_{10}\text{H}_{14}$  to  $[\text{B}_{10}\text{H}_{14}]^{2-}$ . The decaborate complexes  $(\text{NH}_3)_3\text{Yb}[\text{B}_{10}\text{H}_{14}]$ ,  $(\text{CH}_3\text{CN})_6\text{Yb}[\text{B}_{10}\text{H}_{14}]$ ,  $[(\text{CH}_3\text{CN})_x\text{Yb}][\text{B}_{10}\text{H}_{13}][\text{B}_{10}\text{H}_{15}]$ ,  $(\text{NH}_3)_x\text{Eu}[\text{B}_{10}\text{H}_{14}]$ ,  $(\text{CH}_3\text{CN})_x\text{Eu}[\text{B}_{10}\text{H}_{14}]$ , and  $[(\text{CH}_3\text{CN})_x\text{Eu}][\text{B}_{10}\text{H}_{13}][\text{B}_{10}\text{H}_{15}]$  were synthesized from reduction products of  $\text{B}_{10}\text{H}_{14}$  in liquid ammonia by the elemental lanthanides. Reduction products in these reactions were ammonia-solvated powders, insoluble in saturated amines and ethers. Components of these solids were extracted with  $\text{CH}_3\text{CN}$ .

The molecular structure of  $(\text{CH}_3\text{CN})_6\text{Yb}[\text{B}_{10}\text{H}_{14}]$  is shown in Figure 2. It crystallizes as  $(\text{CH}_3\text{CN})_6\text{Yb}[(\mu\text{-H})_2\text{B}_{10}\text{H}_{12}]$  with two additional molecules of  $\text{CH}_3\text{CN}$



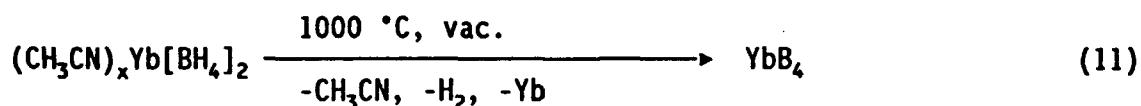
of solvation.<sup>25b</sup> This X-ray structure confirms the presence of the Yb-H-B bridge bonding inferred from <sup>11</sup>B NMR spectra.

### C. Formation of Lanthanide Borides.

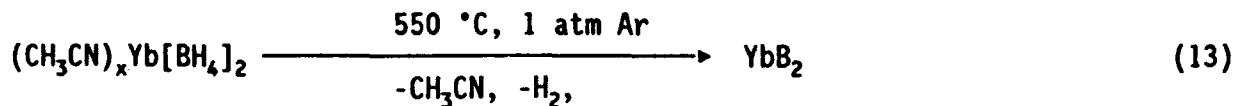
1. Thermal Decomposition of Ln(II) Borohydrides.<sup>25a</sup> When  $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu\text{-H})_3\text{BH}]_2$  and  $(\text{CH}_3\text{CN})_2\text{Eu}[\text{BH}_4]_2$  are heated in vacuum at 200 °C,  $\text{CH}_3\text{CN}$  and  $\text{H}_2$  are evolved, but no boron hydride is produced (Equation (10)). IR spectra



of the resulting solids reveal no ligand stretches. These solids represent an intimate mixture of elemental lanthanide and boron in a precise 1:2 ratio, an ideal starting point for producing a metal boride. Dry solids from the complexes  $(\text{CH}_3\text{CN})_4\text{Yb}[(\mu\text{-H})_3\text{BH}]_2$  and  $(\text{CH}_3\text{CN})_2\text{Eu}[\text{BH}_4]_2$  were heated to 1000 °C in a quartz tube maintained at  $10^{-5}$  Torr (Equations (11) and (12)). At 100 °C  $\text{CH}_3\text{CN}$  is given off; above 150 °C  $\text{H}_2$  evolution occurs; above 450 °C, lanthanide metal sublimes out of both solids.



The resulting materials are shiny-grey solids with a metallic luster. Their X-ray powder patterns revealed  $\text{YbB}_4$  and  $\text{EuB}_6$  to be the only crystalline phases present. We were able to prepare a crystalline  $\text{YbB}_2$  phase by referring to the phase diagram to choose conditions under which  $\text{YbB}_2$  is stable (Equation (13)).<sup>28</sup>



2. Thermal Decomposition of Ln(II) Decaborates. Controlled pyrolyses of  $(CH_3CN)_6Yb[B_{10}H_{14}]$  and  $(NH_3)_xEu[B_{10}H_{14}]$  in vacuum produces Ln(II) complexes of the *closo*-anion  $[B_{10}H_{10}]^{2-}$  (Equation (14)).<sup>27b</sup> These *closo*-complexes



$Ln = Eu, Yb$     $L = NH_3, CH_3CN$

are soluble in  $CH_3CN$  or  $C_5H_5N$ . The  $^{11}B$ -NMR spectrum of  $Yb[B_{10}H_{10}]$  in  $C_5H_5N$  is very similar to that of alkali metal salts of  $[B_{10}H_{10}]^{2-}$ , indicating that this ion is solvent separated in solution. To further investigate the thermal stability of this compound it was heated in a quartz tube. The  $Yb[B_{10}H_{10}]$  slowly evolved  $H_2$  from 300-500  $^\circ\text{C}$ ; no further volatiles were evolved up to 1000  $^\circ\text{C}$ . The X-ray powder pattern of the resulting black powder showed it to be  $YbB_6$ . Amorphous B was probably present as well.  $M(B_{10}H_{10})_3$  complexes ( $M = Ce, Gd$ ) have been thermally decomposed at 1000 - 1200  $^\circ\text{C}$  to form  $CeB_6$  and  $GdB_6$  and amorphous boron.<sup>29</sup>

## V. New Syntheses of Boron Nitride

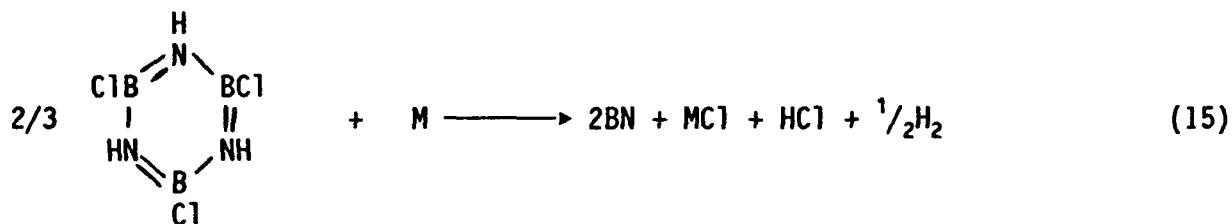
Boron nitride is a well-known ceramic, possessing a number of useful properties.<sup>30,31</sup> Articles composed (wholly or in part) of BN are finding an increasing number of applications. Consequently there is great interest in finding new and improved methods for its production<sup>31</sup>.

Traditional<sup>31-33</sup> routes to boron nitride involve high temperature syntheses. A common method for commercial BN production involves carbothermal reduction of boric acid<sup>31</sup> at temperatures in excess of 1500  $^\circ\text{C}$ , under an atmosphere of  $N_2$ . For production of BN thin films of exceptionally high purity, chemical vapor deposition (CVD) is employed<sup>30,31,34</sup>, with the most widely-used precursors being

$\text{BCl}_3/\text{NH}_3$  and  $\text{BCl}_3/\text{NH}_3/\text{H}_2$  mixtures. Additionally, there has been much recent interest in polymeric preceramic compounds<sup>31,35-37</sup>, where the boron and nitrogen-containing polymer may then undergo thermolysis to yield BN. Described are syntheses that provide high purity boron nitride in potentially useful forms.

#### A. Formation of Boron Nitride from $\text{B}_3\text{Cl}_3\text{N}_3\text{H}_3$

We produced amorphous boron nitride in an unprecedented procedure that involves the reaction of  $\text{B}_3\text{Cl}_3\text{N}_3\text{H}_3$  with the alkali metals (Cs, Rb, K) in the absence of a solvent.<sup>38</sup> The reaction is initiated at 130 - 160 °C; it is vigorous



(M = Cs, Rb, K)

and virtually instantaneous, proceeding with a flash of light. Effectively hydrogen and chlorine are stripped from the  $\text{B}_3\text{N}_3$  core to give amorphous BN. Higher temperatures are required in the reactions of  $\text{B}_3\text{Cl}_3\text{N}_3\text{H}_3$  with K and Rb than with Cs. This method is the most energy efficient preparation of amorphous boron nitride yet devised. The BN is a very finely divided powder. The amorphous product, after removal of alkali metal halide and unreacted  $\text{B}_3\text{Cl}_3\text{N}_3\text{H}_3$ , was converted to the turbostratic form of boron nitride upon heating to 1100 °C. The experimental density of the turbostratic BN is 1.7 g/cm<sup>3</sup>, in good agreement with the accepted value of 1.7-1.8 g/cm<sup>3</sup>. Chemical analyses and XPS spectra confirm the composition BN. Our present maximum yield of BN is about 60%.

Figure (3) shows the X-ray powder pattern of the amorphous BN after removal of  $\text{CsCl}$  and unreacted  $\text{B}_3\text{Cl}_3\text{N}_3\text{H}_3$ , and the powder pattern of turbostratic BN obtained by heating the amorphous BN to 1100 °C. Figure (4) is the infrared

spectrum of turbostratic BN indicating a clean product with no residual OH bonds or BC<sub>1</sub> bonds.

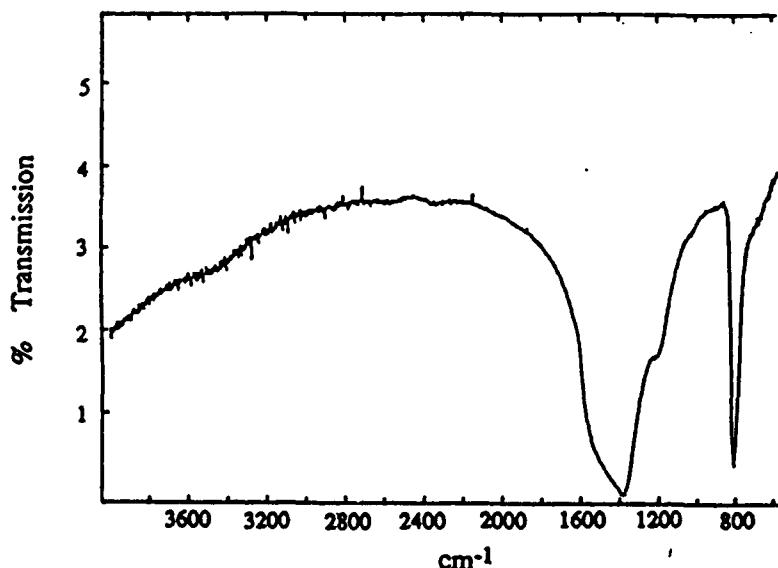
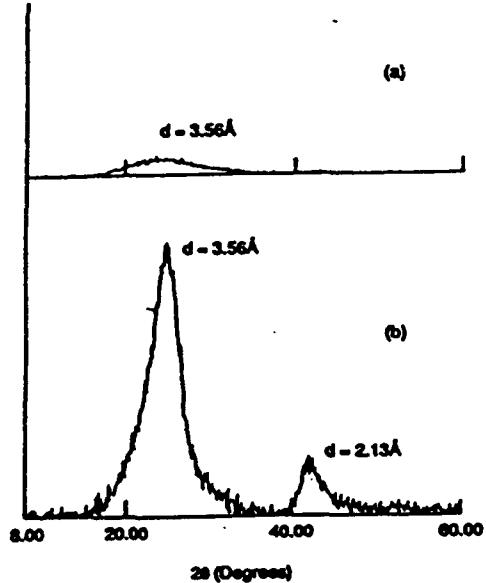


Figure 3. X-ray Powder Patterns:  
a) amorphous boron nitride;  
b) turbostratic boron nitride.

Figure 4. Infrared spectrum of turbostratic boron nitride.

The boron nitride produced need never come in contact with carbon-containing materials, as no solvent is required for the reaction to proceed. Impurities formed in the reaction may be removed by heating and/or washing with water. The main impurity to be removed is the byproduct, CsCl, which is removed by washing with water. It may also be removed by vacuum sublimation at the appropriate temperature (above ca. 600 °C), enabling BN to be prepared which has not been exposed to either water or oxygen. Samples prepared by this procedure are finely divided powders.

### B. Formation of Boron Nitride from $H_3NBH_2Cl$

We prepared  $H_3NBH_2Cl$ , a simple molecular precursor for boron nitride coatings, through the following reaction. Thermolysis of  $H_3NBH_2Cl$  at 1100 °C



produces turbostratic boron nitride.<sup>39</sup> Its X-ray powder pattern and infrared



spectrum are virtually identical to those shown in Figures (3b and 4). Chemical analyses and XPS spectra verify the composition as BN.

Preparation of boron nitride from the thermal decomposition of  $H_3NBH_2Cl$  represents a simple, viable approach to forming BN coatings and possibly thin films through a CVD process. Our synthesis of  $H_3NBH_2Cl$  is much simpler than syntheses of many other precursors that have been employed to produce BN coatings. Furthermore, an ammonia atmosphere is not required during the firing process. Coatings are formed by dipping the object to be coated into an ethereal solution of  $H_3NBH_2Cl$  or by brushing the solution onto the object to be coated. After the solvent has evaporated, firing at 1100 °C produces the turbostratic form of BN. Quartz plates and silicon chips were coated in this manner.

We have found that in the thermal decomposition of  $H_3NBH_2Cl$  only  $H_2$  is given off below 80 °C. A sample of  $H_3NBH_2Cl$  heated to 60 °C for 7 hours eliminated only  $H_2$  gas. The resulting boron-nitrogen containing product analyzed closely for  $B_3N_3Cl_3H_8$ . It appears to be principally two linked cycloborazane rings as indicated on the next page.

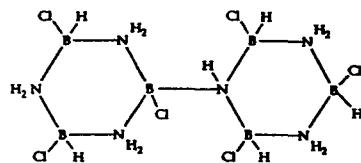


Figure 5. Proposed structure of  $B_3N_3Cl_3H_8$ .

Treatment of this compound with  $LiBH_4$  produces cyclotriborazane,  $B_3H_6N_3H_6$ . Heating of  $B_3N_3Cl_3H_8$  at 88 °C produced additional  $H_2$  but no  $HCl$ . At higher temperatures  $HCl$  was produced.

We obtained a polymeric boron-nitrogen containing material with a parent mass of about 900 by heating  $H_3NBH_2Cl$  in vacuum at a temperature above 150 °C. It is not highly sensitive to moisture and it sublimes in vacuum at elevated temperature. When this material is heated at 1100 °C, BN is formed. This material might be useful for the formation of thin films of BN CVD or for forming films by means of laser ablation.

## VI. A New Boron-Nitrogen-Aluminum Complex

We have observed that the reaction between  $LiAlH_4$  and  $H_3NBH_3$  in a 1:1 molar ratio in THF produces two moles of hydrogen gas and a salt that is assigned the formula  $Li[AlH_2(\mu-NH)(\mu-H)BH_2]$  based on chemical analyses and NMR spectra. The proposed structure of the anion is shown on the next page. The lithium salt is isolated as the thermally stable solid  $Li[AlH_2(\mu-NH)(\mu-H)BH_2] \cdot 0.5THF$ .

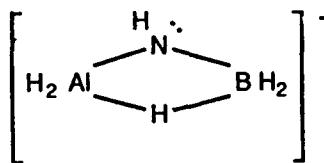


Figure 6. Proposed structure of  $[\text{AlH}_2(\mu\text{-NH})(\mu\text{-H})\text{BH}_2]^-$

## VII. Bibliography

1. a) Shore, S. G.; Toft, M. A. U. S. 4,388,284, 1983. b) Shore, S. G.; Toft, M. A.; Himpsl, F. L. U. S. 4,338,289, 1982.
2. Lawrence, S. H.; Wermer, J. R.; Boocock, S. J.; Banks, M. A.; Keller, P. C.; Shore, S. G. *Inorg. Chem.*, 1986, 25, 367.
3. a) Toft, M. A.; Leach, J. B.; Himpsl, F. L.; Shore, S. G. *Inorg. Chem.* 1982, 21, 1952. b) Leach, J. B.; Toft, M. A.; Himpsl, E. L.; Shore, S. G. *J. Am. Chem. Soc.* 1981, 103, 988.
4. Hosmane, N. S.; Wermer, J. R.; Hong, Z.; Getman, T. D.; Shore, S. G. *Inorg. Chem.* 1987, 26, 3638.
5. Getman, T. D.; Krause, J. A. Niedenzu, P. M.; Shore, S. G. *Inorg. Chem.* 1989, 28, 1507.
6. Getman, T. D.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* 1988, 27, 2398.
7. Getman, T. D.; Shore, S. G. *Inorg. Chem.* 1988, 27, 3439.
8. Getman, T. D.; Deng, H.-B.; Hsu, L.-Y.; Shore, S. G. *Inorg. Chem.* 1989, 28, 3612.
9. a) Walker, F. E.; Wasley, R. J. U.S. 4304,614, 1981. b) Capellos, C.; Iyer, S. *NATO Adv. Study Inst. Ser., Ser. C* 1981, C 71, 401. (c) Walker, F. E.; Wasley, R. J. U.S. 4,196,05, 1980.
10. a) Tamblyn, W. H.; Aquadro, R. E.; Deluca, O. D.; Weingold, D. H.; Dao, T. V. *Tett. Lett.* 1983, 24, 4955. b) Tamblyn, W. H.; Weingold, D. H.; Snell, E. D.; Waltermire, R. E. *Tett. Lett.* 1982, 23, 3337.
11. Komura, M.; Anon, K.; Nagasawa, K.; Sumimoto, S. *Chem. Express* 1987, 2, 173.
12. Hall, I. H.; Brotherton, R. H. U.S. 4,672,060, 1987.

13. a) Gilbert, K. B.; Boocock, S. K.; Shore, *Comprehensive Organometallic Chemistry*, Eds, Wilkinson, G.; Stone, F. G. A.; Abel, E. 1982, Chapt 41.1, and references therein.

14. a) Brelochs, B.; Binder, H. *Z. Naturforsch. B Chem. Sci.* 1988, 43, 648. b) Brelochs, B.; Binder, H. *Angew. Chem.* 1988, 100, 270. c) Wolfer, K.; Hausen, H. D.; Binder, H. *Z. Naturforsch. B Anorg. Chem, Org. Chem.* 1985, 40B, 235. d) Dunks, G. B.; Ordonez, K. D. *Inorg. Chem.* 1978, 17, 1514. e) Ryschkewitsch, G. E.; Miller, V. H. *J. Am. Chem. Soc.* 1975, 97, 6258.

15. a) Gaines, D. F.; Kunz, J. C. *Inorg. Chem.* 1988, 27, 1893. b) Gaines, D. F.; Coons, D. E. *Inorg. Chem.* 1986, 25, 364.

16. a) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* 1980, 19, 3482. b) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* 1979, 18, 3294.

17. Shevchenko, Y. N.; Fesenko, A. V.; Nazarova, T. M.; Biryukovich, O. K.; Yatsimirskii, K. B.; Ogenko, U. M.; Sleasarenko, Y. N.; Naprasnaya, S. V.; Larikov, E. I.; Svitsyn, R. A. *Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Zhaki* 1984, (31), 78.

18. Hough, W.V.; Edwards, L.J.; McElroy, A. D. *J. Am. Chem. Soc.* 1956, 78, 689.

19. a) Dewkett, W. J.; Grace, M.; Beall, H. *Inorg. Syn.* 1974, 15, 115. b) Amberger, E.; Gut, E. *Chem. Ber.* 1968, 101, 1200.23.

20. Kodama, G.; Parry, R. W. *J. Am. Chem. Soc.* 1960, 82, 6250.

21. a) Depoy, R. E.; Kodama, G. *Inorg. Chem.* 1988, 27, 1836. b) Toft, M. A.; Leach, J. B.; Himpsl, F. L.; Shore, S. G. *Inorg. Chem.* 1982, 21, 1952.

22. Hill, T. G.; Godfroid, R. A.; White, J. P. III; Shore, S. G. *Inorg. Chem.* 1991, 30, 2952.

23. Browning, E. *Toxicity of Industrial Metals*, 2nd ed., Appleton-Century-Crofts, NY, 1969, pp. 317-322.

24. Matkovich, V. I. Ed. *Boron and Refactory Borides* Springer-Verlag New York, 1977.

25. a) White, J. P. III; Deng, H.-B.; Shore, S. G. *Inorg. Chem.* 1991, 30, 2337. b) White, J. P. III; Deng, H-B; Shore, S. G. *J. Am. Chem. Soc.* 1989, 111, 8946.

26. Marks, T. J.; Kolb, J. R. *Chem. Rev.* 1977, 77, 263.

27. Toeniskoetter, R.H. Ph.D. Dissertation, St. Louis University 1958, St. Louis, Mo. (Diss. Abstr. 1959, 20, 879).

28. *Binary Alloy Phase Diagrams* Massalski, T. B., Ed., 1986, American Society for Metals, Vol. 1, 354.

29. Itoh, H.; Tsuzuki, Y.; Yogo, T.; Naka, S. *Mat. Res. Bull.* 1987, 22, 1259.

30. a) Meller, A. *Gmelin Handbuch der Anorganische Chemie, Boron Compounds*, 2nd Suppl. 1983, 1, 304. b) Meller, A. *Gmelin Handbuch der Anorganische Chemie, Boron Compounds*, 3rd Suppl. 1988, 3, 1.

31. Paine, R. T.; Narula, C. K. *Chem. Rev.* 1990, 90, 73 and references therein.

32. O'Connor, T. E. *J. Am. Chem. Soc.* 1962, 84, 1753.

33. Economy, J.; Anderson, R. *Inorg. Chem.* 1966, 5, 989.

34. Singh, R. N. *Proc. Electrochem. Soc.* 1987, 87-88, 543.

35. Fazen, P. J.; Beck, J. S.; Lynch, A. T.; Remsen, E. E.; Sneddon, L. G. *Chem. Mater.* 1990, 2, 96.

36. Narula, C. K.; Lindquist, D. A.; Fan, M.-F.; Borek, T. T.; Duesler, E. N.; Datye, A. K.; Schaeffer, R.; Paine, R. T. *Chem. Mater.* 1990, 2, 377.

37. a) Narula, C. K.; Schaeffer, R.; Datye, A. K.; Borek, T. T.; Rapko, B. M.; Paine, R. T. *Chem. Mater.* 1990, 2, 384. b) Beck, J. S.; Albani, C. R.; McGhie; McGhie, A. R.; Rothman, J. B.; Sneddon, L. G. *Chem. Mater.* 1989, 1, 433.; c) Kazimiera, J. L. Paciorek; Masuda, S. R.; Kratzer, R. H.; Schmidt, W. R. *Chem. Mater.* 1991, 3, 88.

38. Shore, S. G.; Dolan, S. E. U. S. 5,053,365, 1991.

39. Shore, S. G., Niedenzu, P. M.; Degrafenried, A. L. U. S. Pending.

## VIII. PUBLICATIONS, PATENTS, DISSERTATIONS

### A. Publications

"Synthesis of the New Boron Hydride *nido*-Undecaborane(15),  $B_{11}H_{15}$ , and the X-Ray Structure of its Conjugate Base Tetradecahydroundecaborate(1-),  $[B_{11}H_{14}]^-$ " Getman, T. D.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* 1988, 27, 2398.

" $[B_9H_{13}]^{2-}$  an *arachno*- $[B_nH_{n+4}]^{2-}$  Dianion; Synthesis, Characterization, and Molecular Structure" Getman, T. D.; Krause, J. A.; Niedenzu, P. M.; Shore, S. G. *Inorg. Chem.* 1989, 28, 1507.

"Syntheses of *closo*-Methylphosphadodecaborane(11),  $B_{11}H_{11}PCH_3$  and *nido*-7-methylphosphaundecaborane(12),  $B_{10}H_{12}PCH_3$ , from the  $[B_{11}H_{13}]^{2-}$  Anion and their Molecular Structures" Getman, T. D.; Deng, H.-B.; Hsu, L.-Y.; Shore, S. G. *Inorg. Chem.* 1989, 28, 3612.

"Synthesis of Divalent Lanthanide Tetradecahydrodeca- and Decahydrodeca-borates: The X-Ray Crystal Structure of  $(CH_3CN)_6Yb(\mu-H)_2-B_{10}H_{12}\cdot CH_3CN$ " White, J. P. III; Deng H.-B.; Shore, S. G. *J. Am. Chem. Soc.* 1989, 111, 8946.

"Borohydride Complexes of Eu(II) and Yb(II) and Their Conversion to Metal Borides; Structure of  $(L)_4Yb[BH_4]_2$  ( $L = CH_3CN, C_5H_5N$ )" White, J. P. III; Deng, H.-B.; Shore, S. G. *Inorg. Chem.* 1991, 30, 2337.

"Reduction of  $BH_3\cdot THF$  by Alkali (K, Rb, Cs) and Ytterbium Amalgams to Form Salts of  $[B_3H_8]^-$ ; A Simple Procedure for the Synthesis of Tetraborane(10)" Hill, T. G.; Godfroid, R. A.; White, J. P. III; Shore, S. G. *Inorg. Chem.* 1991, 30, 2952.

"Coordination Complexes of Divalent Lanthanides (Sm(II), Eu(II), Yb(II)) with Decaborates; Evidence for Lanthanide Hydrides En Route to Lanthanide Borides" White, J. P. III; Shore, S. G. *Inorg. Chem.* Submitted.

### B. Patents

"Method for the Low Temperature Preparation of Amorphous Boron Nitride Using Alkali Metal and Haloborazines" Shore, S. G.; Dolan, S. E. U. S. 5,053,365, 1991.

"Method for the Preparation of Boron Nitride Using Ammonia-Monohaloborane" Shore, S. G.; Niedenzu, P. M.; DeGraffenreid, A. L. U. S. Pending.

### C. Dissertations

"The Reaction of Alkali Metals and Trihaloborazines. A New Method to Produce Amorphous Boron Nitride and the Preparation of Boron-Nitride Polymers" by Shawn Dolan. M.S. Dissertation, 1989.

"Studies of Polyboron Hydride Anions and Amine-Borane" by Phillip Niedenzu. Ph.D. Dissertation, 1990.

"Synthesis and Characterization of Divalent Lanthanide ( $Ln^{2+} = Sm, Eu, Yb$ ) Coordination Complexes with Boron Hydride and Transition Metal Carbonyl Anions; The Formation of Metallic Films and Metal Borides from Complex Precursors" by James White. Ph. D. Dissertation, 1990.

"Alkali and Lanthanide Metal Salts of the Octahydrotriborate(1-) Ion" by Robert A. Godfroid. M.S. Dissertation 1991.

## **IX. PARTICIPATING SCIENTIFIC PERSONNEL**

Dr. Sheldon Shore  
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Dr. James White (PhD, 1990)

## **X. INVENTIONS**

**"Method for the Low Temperature Preparation of Amorphous Boron Nitride Using Alkali Metal and Haloborazines"**

**"Method for the Preparation of Boron Nitride Using Ammonia-Monohaloborane"**